AD-A040 718 AEROSPACE CORP EL SEGUNDO CALIF AEROPHYSICS LAB F/G 7/4
ANALYTICAL PHOTON CATALYSIS: MEASUREMENT OF BI CONCENTRATIONS T--ETC(U)
APR 77 G A CAPELLE, D G SUTTON F04701-76-C-0077
UNCLASSIFIED TR-0077(2240)-1 SAMSO-TR-77-96 NL

1 OF 1
AD A040718

END

DATE FILMED
7-77

REPORT SAMSO-TR-77-96

(12)
B.S.

Analytical Photon Catalysis: Measurement of Bi Concentrations to $10^4/cm^3$

Aerophysics Laboratory
The Ivan A. Getting Laboratories
The Aerospace Corporation
El Segundo, Calif. 90245

19 April 1977

Interim Report

Prepared for
SPACE AND MISSILE SYSTEMS ORGANIZATION
AIR FORCE SYSTEMS COMMAND
Los Angeles Air Force Station
P.O. Box 92960, Worldway Postal Center
Los Angeles, Calif. 90009

This interim report was submitted by The Aerospace Corporation, El Segundo, CA 90245, under Contract No. F04701-76-C-0077 with the Space and Missile Systems Organization, Deputy for Advanced Space Programs, P.O. Box 92960, Worldway Postal Center, Los Angeles, CA 90009. It was reviewed and approved for The Aerospace Corporation by W. R. Warren, Jr., Director, Aerophysics Laboratory. Lieutenant Dara Batki, SAMSO/YAPT, was the project officer for Advanced Space Programs.

This report has been reviewed by the Information Office (OI) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

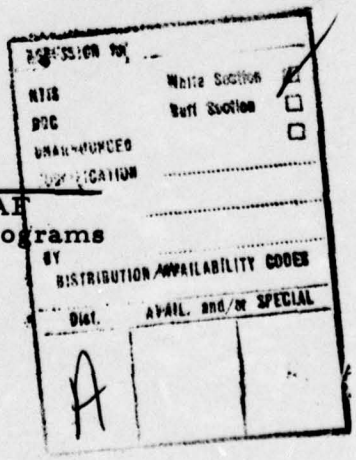
This technical report has been reviewed and is approved for publication.

Dara Batki
Dara Batki
Project Officer

J Gassmann
Joseph Gassmann, Major USAF

FOR THE COMMANDER

Floyd R Stuart
Floyd R. Stuart, Colonel, USAF
Deputy for Advanced Space Programs



UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER: SAMSO-TR-77-96	2. GOVT ACCESSION NO. / 3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle): ANALYTICAL PHOTON CATALYSIS: MEASUREMENT OF BI CONCENTRATIONS TO 10^4/cm^3 ≠ 10,000 cu/cm.	5. TYPE OF REPORT & PERIOD COVERED: Interim ≠ rept.
	6. PERFORMING ORG. REPORT NUMBER: TR-0077(2240)-1
7. AUTHOR(s): Gene A. Capelle and David G. Sutton	8. CONTRACT OR GRANT NUMBER(s): F04701-76-C-0077
9. PERFORMING ORGANIZATION NAME AND ADDRESS: The Aerospace Corporation, El Segundo, Calif. 90245	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS: Space and Missile Systems Organization, Air Force Systems Command, Los Angeles, Calif. 90009	12. REPORT DATE: 19 April 1977
	13. NUMBER OF PAGES: 15
14. MONITORING AGENCY NAME & ADDRESS *(if different from Controlling Office)*: 17 p.	15. SECURITY CLASS. *(of this report)*: Unclassified
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT *(of this Report)*

Approved for public release; distribution unlimited

17. DISTRIBUTION STATEMENT *(of the abstract entered in Block 20, if different from Report)*

18. SUPPLEMENTARY NOTES

19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

Active Nitrogen
Bismuth
Concentration Measurements
Emission Spectroscopy
Trace Element Analysis
Vapor Pressure Curves

A (superscript + 3 Sigma (+) subscript u)

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

A new analytic technique was developed to determine quantitatively the concentration of gas-phase species at concentrations well below the capabilities of atomic absorption and mass spectroscopy. The method involves injecting an excess of an energetic metastable species, $N_2(A^3\Sigma_u^+)$ in this experiment, into a gas stream containing the species to be measured, Bi in this case. Energy transfer from the metastable to the sample species results in excitation and subsequent rapid emission of light. The intensity of the light emitted at the wavelengths characteristic of the sample species is a function → next page

DD FORM 1473 (FACSIMILE)

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

409367

19. KEY WORDS (Continued)

20. ABSTRACT (Continued)

of, and hence a measure of, the concentration. Concentrations as low as $1.5 \times 10^4/cm^3$ were measured. Greater sensitivity is possible with more efficient optical detection.

15000 / cu. cm.

PREFACE

The authors thank Professor Sidney Benson for pointing out the inherent high sensitivity of this technique and for his subsequent enthusiastic support and advice.

CONTENTS

FIGURES

I. INTRODUCTION

Until now, no known method has existed that conveniently allowed the quantitative detection of atomic and molecular species at concentrations below $10^8/cm^3$. Atomic absorption is limited to concentrations greater than 10^8 atoms/cm^3.[1] Mass spectroscopy is generally less sensitive than atomic absorption. The doppler-free, two-photon excited fluorescence method is theoretically capable of detecting 10^5 molecules/cm^3, but only when favorable absorption cross sections and radiative lifetimes are assumed.[2] The resonantly enhanced two-photon absorption method can detect 10^2 atoms/cm^3, but the absorber must have a fortuitous set of energy levels, and two narrow-band, tunable dye lasers are required.[3] Detection of 10^2 Na atoms/cm^3 has been demonstrated with the use of a single-photon laser fluorescence method.[4] For many species, however, this method would require frequency-doubled dye lasers, even more sophisticated dye-laser frequency-mixing devices, or the use of pulsed dye lasers, which reduce the detection sensitivity. In addition, methods that employ dye lasers are by comparison relatively costly. This technique (based on an idea of Capelle) provides relatively simple quantitative detection of sample particles in a gas stream at very low concentrations. It is a general technique and is applicable to many atomic and molecular species.[5-7]

The method consists of monitoring the fluorescence intensity from a sample species, S, excited by energy transfer from a metastable species, M^*.

The kinetics are summarized as follows:

$$M^* + S \xrightarrow{k} M + S^* \qquad (1)$$

$$S^* \xrightarrow{1/\tau} S + h\nu \qquad (2)$$

where the asterisk implies electronic excitation. If the metastable is in excess and the radiative transition, Reaction (2), is fully allowed ($\tau \sim 10^{-8}$ sec), then pseudo first-order kinetics obtain, with Reaction (1) representing the rate controlling step. Under these conditions, the fluorescence intensity per unit volume, I, is related to the sample species concentration,

$$I = k[M^*][S] \qquad (3)$$

and the measurement of I determines the relative sample concentration. For the determination of absolute concentrations, the value of k and $[M^*]$ must be known or the system must be calibrated by measuring [S] with a suitable alternative technique at some conveniently high concentration. The rate constant, k, is large ($> 10^{-13}$ cm^3/sec) for transfer from metastable $N_2(A^3\Sigma_u^+)$ (Ar, He, and other metastables should also work) to many atomic acceptors.[8] Since this species can be prepared by discharge techniques at concentrations of $10^{13}/cm^3$, extremely small concentrations of sample particles can result in large fluorescence intensities. By the use of sensitive photon-counting techniques on samples with large transfer rate constants, detection of < 100 particles/cm^3 is feasible. In this scheme, the sample particles may undergo

the excitation-emission cycle repeatedly. They are the catalytic agent for the production of photons from the energy stored in the metastable. This characteristic accounts for the high sensitivity of the method. Detection of the radiation from this process gives the experimentalist a very sensitive technique for qualitative and quantitative analyses.

II. EXPERIMENT

The apparatus is shown schematically in Fig. 1. It consists of a vertical section of quartz tubing 9 cm in diameter. An electrically heated metal vapor furnace is attached to the bottom of the quartz tube, and a 60 liters/sec pump, attached at the top of the quartz tube, provides the means to evacuate the system. Argon injected through the bottom of the furnace assembly entrains the flow of atomic Bi from the furnace and carries it into the quartz observation section. In this section, the concentration of Ar ($\geq 10^{16}/cm^3$) is much greater than the bismuth concentration. A thermocouple placed in contact with the bismuth in the furnace allows direct measurement of the metal atom source temperature.

A ring-shaped quartz gas injector was inserted into the apparatus at the junction of the furnace assembly and quartz flow tube. Through this injector, active nitrogen was introduced into the Ar-Bi stream. The active nitrogen, consisting primarily of N atoms, $N_2(A^3\Sigma_u^+)$, and ground-state N_2, was prepared upstream of the injector by passing N_2 gas through a 70-W microwave discharge. The region of the quartz flow tube $\sim$ 5 cm above the active nitrogen injector was monitored photoelectrically with a 1P28 phototube attached to a 1/2 m monochromator. A hollow cathode Bi lamp was placed on the opposite side of the flow tube and at the same height as the monochromator entrance slits. It was used as a line source for the atomic absorption measurements to calibrate the fluorescence intensity measurements with respect to Bi vapor concentration.

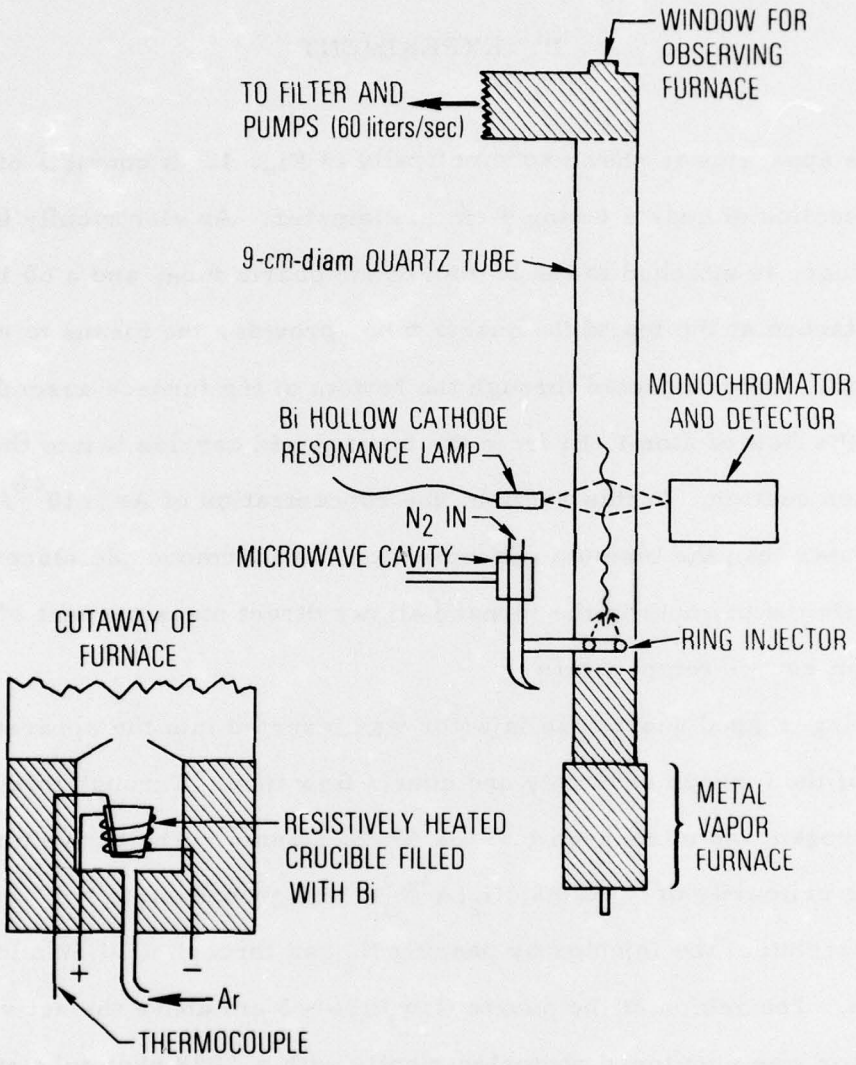


Fig. 1. Apparatus

III. RESULTS AND DISCUSSION

The Ar and N_2 flows (10^{21}/sec and 2×10^{20}/sec, respectively) were adjusted to give a total pressure of 0.5 Torr. With the microwave generator set to deliver 70 W to the N_2 flow, a pale straw-colored glow was observable downstream of the injector. The furnace was then set to a given temperature, and the resulting atomic Bi emission was measured. This consisted predominantly of the 3068-Å line from the $^4P_{1/2} \rightarrow {}^4S^0_{3/2}$ transition. However, several lines were recorded at each temperature. In Fig. 2, the intensity of the 3068-Å line (left-hand scale) at several temperatures is plotted against $10^4/T(K)$. The slope of the resulting straight line is the same as a plot (suggested from a critical review of the literature) of the log of the Bi equilibrium vapor pressure versus $10^4/T(K)$. Evidently, the fluorescence intensity from the excited Bi in the observation zone is proportional to the vapor pressure of ground-state metal that would result from the furnace temperature in an equilibrium situation. Similar plots were made from the intensity data of eight different Bi emission lines, and all were linear with the same slope over the temperature range in which they could be observed.

At the higher temperatures, the Bi density was sufficient to make atomic absorption measurements by means of the 3068-Å line from the Bi hollow cathode lamp,[9] thereby directly determining the Bi-atom ground-state concentration. The results for several values of the source temperature are also plotted in Fig. 2. These points and the slope from Ref. 10 were used to calibrate the graph, giving the scale on the right-hand side.[11] Bismuth

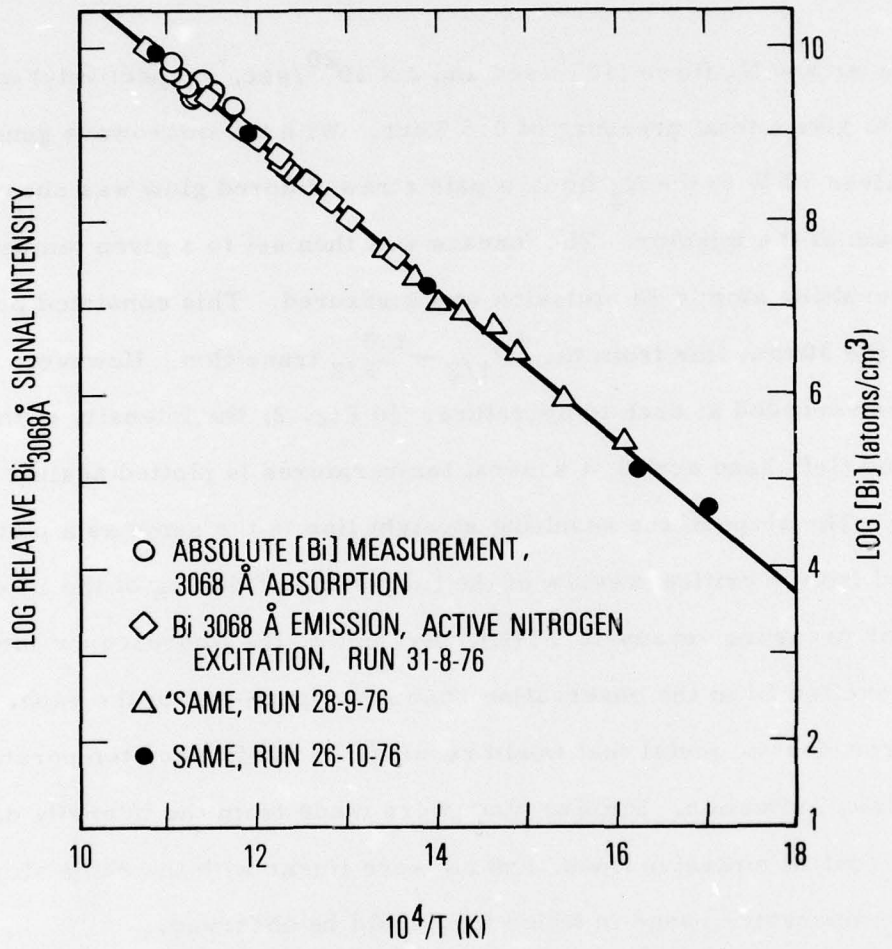


Fig. 2. Plot of Bi Concentration as a Function of 10^4/T(K)

vapor concentrations down to $1.5 \times 10^4/cm^3$ were measured. With refinements of the method, it should be possible to detect Bi and many other species at concentrations of $100/cm^3$ or less. Experiments to this end and to demonstrate the generality of the method are in progress.

Because of its extremely high sensitivity and relative simplicity, the method described here has numerous immediate applications and many more potential applications. It should be relatively easy to measure vapor-pressure curves accurately for most of the elements over a range of more than eight orders of magnitude. The method offers a reasonably simple means of monitoring and analyzing exhaust and stack emissions. Other possible applications include solid-state-device analysis (for trace impurities), forensic analysis, e.g., of hair or explosives, and nondestructive material and alloy analysis.

REFERENCES

1. J. D. Winefordner and T. J. Vickers, Anal. Chem. 42, 206R (1970).
2. Jerry Gelbwachs, Appl. Opt. 15, 2654 (1976).
3. J. E. Bjorkholm and P. F. Liao, Optics Comm. 18, 4 (1976).
4. W. M. Fairbank, Jr., T. W. Hänsch, and A. L. Schawlow, J. Opt. Soc. Amer. 65, 199 (1975).
5. L. F. Phillips, Can. J. Chem. 41, 2060 (1963).
6. W. R. Brennen and G. B. Kistiakowsky, J. Chem. Phys. 44, 2695 (1966
7. S. Rosenwaks and H. P. Broida, J. Opt. Soc. Am. 66, 75 (1976).
8. A. Nelson Wright and Carl A. Winkler, Active Nitrogen, Academic Press, New York (1968).
9. The oscillator strength used for the absorption measurements at 3068 Å was taken from the work of P. A. Rice and D. V. Ragone, J. Chem. Phys. 42, 701 (1965). The lifetime measurements of P. T. Cunningham and J. K. Link, J. Opt. Soc. Amer. 57, 1000 (1967) support the value of Rice and Ragone.
10. An. N. Nesmeyamov, Vapour Pressure of the Elements, translated and edited by J. I. Carasso, Academic Press, New York (1963).
11. The absorption measurements described here and used to calibrate Fig. 2 were made with the microwave power on (under the same conditions as the fluorescence measurements). Two of the sources cited in

Reference 10, however, indicate that, at a crucible temperature of 600 to 700°C, the effluent bismuth vapor should exist as roughly equal parts of monomer and dimer. In order to assess the role of dimer formation, atomic absorption measurements were made at 3068 Å as a function of crucible temperature and microwave power. At a crucible temperature of 640°C, the ground state Bi monomer concentration increased by a factor of three when the microwave power was increased from 0 to 20 W. Further increases in microwave power effected no additional change. Evidently, the bismuth vapor does exist as both monomer and dimer in the gas flow at the proportions expected from the crucible temperature, and the active nitrogen is effective in dissociating virtually all of the dimer. The mechanism may involve either N-atom attack on the dimer or dissociative excitation transfer.

THE IVAN A. GETTING LABORATORIES

The Laboratory Operations of The Aerospace Corporation is conducting experimental and theoretical investigations necessary for the evaluation and application of scientific advances to new military concepts and systems. Versatility and flexibility have been developed to a high degree by the laboratory personnel in dealing with the many problems encountered in the nation's rapidly developing space and missile systems. Expertise in the latest scientific developments is vital to the accomplishment of tasks related to these problems. The laboratories that contribute to this research are:

Aerophysics Laboratory: Launch and reentry aerodynamics, heat transfer, reentry physics, chemical kinetics, structural mechanics, flight dynamics, atmospheric pollution, and high-power gas lasers.

Chemistry and Physics Laboratory: Atmospheric reactions and atmospheric optics, chemical reactions in polluted atmospheres, chemical reactions of excited species in rocket plumes, chemical thermodynamics, plasma and laser-induced reactions, laser chemistry, propulsion chemistry, space vacuum and radiation effects on materials, lubrication and surface phenomena, photosensitive materials and sensors, high precision laser ranging, and the application of physics and chemistry to problems of law enforcement and biomedicine.

Electronics Research Laboratory: Electromagnetic theory, devices, and propagation phenomena, including plasma electromagnetics; quantum electronics, lasers, and electro-optics; communication sciences, applied electronics, semiconducting, superconducting, and crystal device physics, optical and acoustical imaging; atmospheric pollution; millimeter wave and far-infrared technology.

Materials Sciences Laboratory: Development of new materials; metal matrix composites and new forms of carbon; test and evaluation of graphite and ceramics in reentry; spacecraft materials and electronic components in nuclear weapons environment; application of fracture mechanics to stress corrosion and fatigue-induced fractures in structural metals.

Space Sciences Laboratory: Atmospheric and ionospheric physics, radiation from the atmosphere, density and composition of the atmosphere, aurorae and airglow; magnetospheric physics, cosmic rays, generation and propagation of plasma waves in the magnetosphere; solar physics, studies of solar magnetic fields; space astronomy, x-ray astronomy; the effects of nuclear explosions, magnetic storms, and solar activity on the earth's atmosphere, ionosphere, and magnetosphere; the effects of optical, electromagnetic, and particulate radiations in space on space systems.

THE AEROSPACE CORPORATION
El Segundo, California